

FUNDAMENTALS OF CHEMICAL BEHAVIOR IN ANHYDROUS NITRIC ACID

Zeitschrift fuer Anorganische Chemi, Aug 1948

24 July 1950

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[A digest]

Anhydrous nitric acid resembles in its properties non-aqueous solvents which behave similarly to water (for instance, ammonia or sulfur dioxide). It dissolves, just as water does, a great number of substances, particularly inorganic compounds. The resulting solutions conduct an electrical current well, while the solvent alone is a rather poor conductor. The solutes are present in a dissociated form. In as far as nitric acid conducts an electrical current at all, the following dissociation scheme is responsible for that property:



Anhydrous nitric acid forms solvates which correspond to hydrates, but only the existence of solvates of nitrates has been established. Reactions similar to neutralization in aqueous solution are comparatively rare in nitric acid. The acid analogon [i.e., a substance which behaves as an acid in nitric acid] perchloric acid interacts in nitric acid with the alkali analogon potassium nitrate under formation of a salt and of a molecule of the solvent:



Anhydrous sulfuric acid in the medium in question is also capable of reactions similar to neutralization. Its salts undergo solvolysis at elevated temperatures, however.

The conductivities of sodium nitrate, potassium nitrate, and tetramethylammonium nitrate increase sharply with increasing concentration in nitric acid. This means that the alkali analogons in question are still dissociated to a considerable degree at high concentrations. In view of the fact that the specific conductivities of nitrates run parallel to their solubilities, some sort of relationship between these two properties may be assumed to exist. The only sparingly soluble uranyl nitrate shows an increase of conductivity with increasing concentrations which is so low as to be imperceptible. If comparisons are drawn between

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between the conductivity of nitrates in nitric acid and, to take a typical instance, the conductivity of alkali chlorides in water, one must consider that the range of the liquid state lies between 0°C and 100°C for water, while the same range lies between minus 41°C and plus 86°C in the case of nitric acid. Under the circumstances conductivity measurements carried out in nitric acid at plus 20°C correspond to conductivities determined in water at plus 50°C . On carrying out this type of extrapolation in the case of alkali chlorides dissolved in water ~~as compared with alkali nitrates or tetraethylammonium nitrate~~ dissolved in nitric acid, values of ^{the} same order are obtained for conductivities. I.e., the conductivities have equally high values ⁱⁿ for both solvents.

Conductivities in nitric acid of the acid analogs perchloric acid, sulfuric acid, nitrosyl sulfuric acid, and picric acid were also determined. Perchloric acid and nitrosyl sulfuric acid behave in nitric acid like normal electrolytes. Their specific conductivity, although not ^{very} high, increases with rising concentrations. In the case of sulfuric acid, there is a decrease of conductivity at first with a minimum at a concentration of 0.2 mols, and a subsequent increase leading to a normal conductivity-concentration curve at higher concentrations. The specific conductivities of picric acid in nitric acid show a similar behavior, so that the curve goes downward until a concentration of approximately 0.15 mols is reached ~~no~~ values corresponding to higher concentrations have apparently been determined by the authors. On extrapolating the equivalent conductivities for the acids in a manner similar to that described in the case of the base analogs, the same conditions were found to exist here.

Perchloric acid is a relatively strong acid in nitric acid solution. It can be titrated conductivometrically with potassium nitrate. In the course of the titration, potassium perchlorate is precipitated. Conversely, potassium nitrate can be titrated in nitric acid solution with perchloric acid.

Sulfuric acid, which is a weaker acid than perchloric in nitric acid solution, can be used to titrate potassium nitrate in that solvent. The intersection of the two straight lines representing the conductivity-concentration dependence is very clear at the point corresponding to KHSO_4 , because of the sharply diverging slopes, but the point corresponding to K_2SO_4 is not very distinct, the two

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lines forming an angle close to 180° at that point. Both KHSO_4 and K_2SO_4 are easily soluble in concentrated nitric acid. The reverse titration, that of sulfuric acid with potassium nitrate, also results in a conductivity-concentration curve showing two intersection points.

Nitrosyl sulfuric acid is easily soluble in nitric acid and lies somewhere between perchloric and sulfuric acids as far as acid strength in that solvent is concerned. Attempts at a conductivometric titration of nitrosyl sulfuric acid with potassium nitrate led to the conclusion that solvolysis of the potassium salt formed by double decomposition probably occurs.

Aside from perchloric acid and sulfuric acid, other acids (either inorganic or organic) which behave in a similar manner in nitric acid solution (i.e., can be neutralized) have not been found. The salts of all other acids, as will be shown in a subsequent communication, undergo solvolysis in nitric acid. In this respect anhydrous nitric acid resembles anhydrous hydrofluoric acid, a medium in which acids weaker than the perchloric or sulfuric acid analogs also do not exist and, those of medium strength are not known.

This is a communication from the Chemical Institute of the University of Greifswald, submitted for publication on March 12, 1948.⁷

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